

EPITAXIAL FILMS

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Field of the Invention

The present invention relates broadly to the growth of epitaxial II-VI semiconductor films. The invention will be described herein with reference to the growth of epitaxial zinc sulfide (ZnS) on silicon (Si) (111) substrates, but it will be appreciated that the invention does have broader applications relating to growth of epitaxial II-VI semiconductor films of different materials and/or on different substrates.

Background of the Invention

Films that grow with singular crystallographic orientation in all directions are referred to as epitaxial films. This has to be contrasted with poly-crystalline thin films, which include a large number of crystallites but with variable orientations with respect to each other.

Epitaxial thin films have been produced using a variety of different techniques, including molecular beam epitaxy (MBE), vapour phase epitaxy (VPE) and atomic layer epitaxy (ALE). However, a common characteristic of those techniques is that the epitaxial film growth requires multiple sources for the film elements, for example separate sources for zinc (Zn) and sulphur (S) are required for the epitaxial growth of ZnS films. Therefore, such techniques can have the disadvantage of being rather complex processes, during which a large number of variables must be controlled. This often results in high costs associated with the operation of machines for epitaxial film growth.

Epitaxial thin films are desirable for a large number of applications including light emitting layers for diodes, as active layers in optical/electro-optical thin film devices and as coatings. In this application, the single-crystal like characteristics of epitaxial films are utilised, which are typically superior to the characteristics of polycrystalline films.

Summary of the Invention

In accordance with a first aspect of the present invention there is provided an epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapour deposition.

5 In one embodiment, the epitaxial film comprises ZnS. Preferably, the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

10 In another preferred embodiment, the ZnS is grown using  $\text{Zn}(\text{S}_2\text{CNR}_2)_2$ , where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition. The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

15 In accordance with a second aspect of the present invention there is provided a process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial zinc-based II-VI semiconductor film on a substrate.

20 In one embodiment, the epitaxial film comprises ZnS. In one preferred embodiment the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapour deposition.

25 In another preferred embodiment, the ZnS is grown using  $\text{Nz}(\text{S}_2\text{CNR}_2)_2$ , where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition. The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

30 Preferably, the substrate comprises a silicon (111) substrate. In accordance with a third aspect of the present invention, there is provided a substrate coated with a coating comprising an epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapour deposition.

35 Preferably, the substrate comprises silicon (111). In one embodiment, the epitaxial film comprises ZnS.

In accordance with a fourth aspect of the present invention, there is provided a process for growing an epitaxial zinc-based II-VI semiconductor film, the process comprising the steps of cleaning a substrate, heating the substrate to a deposition temperature, the sublimation of a single source chemical vapour deposition precursor;

the pyrolysis of the precursor molecules on the heated substrate; and

the formation of the epitaxial film on the heated substrate.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS. Preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings.

#### Brief Description of the Drawings

Figure 1 is a schematic drawing of a deposition chamber embodying the present invention.

Figure 2 shows angle dependent X-ray photoelectron defraction measurements of epitaxial films embodying the present invention.

Figure 3 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 4 shows an X-ray photoelectron spectroscopy wide scan of a ZnS film embodying the present invention.

Figure 5 shows an angle dependent X-ray photoelectron defraction measurements of a ZnS film after sputtering.

Figure 6 shows energy dependent X-ray photoelectron defraction measurements of an epitaxial film embodying the present invention.

Figure 7 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 8 is a schematic drawing illustrating the formation of an epitaxial film embodying the present invention.

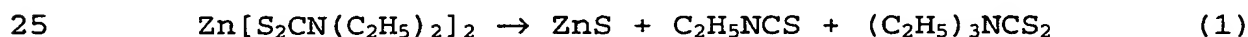
Figure 9 is a block diagram illustrating the growth of epitaxial films embodying the present invention.

Figure 10 is a schematic diagram illustrating a device application embodying the present invention.

## 5 Detailed Description of the Preferred Embodiments

In Figure 1, a high vacuum deposition chamber 10 (base pressure  $10^{-7}$  Torr) comprises a resistively heated Knudsen cell 12 loaded with a zinc diethyldithiocarbamate precursor powder (not shown) for the single source chemical vapour deposition (SSCVD). A silicon Si(111) substrate 19 is mounted on a sample holder 16 on a heater 100 and the epitaxial film (not shown) is formed on the substrate 19. The chamber 10 further comprises a view port 11, a port 13 to which a vacuum pump (not shown) is connected and a flexible flange 15 as part of a x,y,z manipulator 17 for the heater 100.

As illustrated in Figure 8, sublimed zinc diethyldithiocarbamate molecules 80 impinge on the heated substrate 19. In the diethyldithiocarbamate molecules 80, the zinc atom is in a similar environment to that of zinc in crystalline ZnS. The SSCVD growth of the ZnS epitaxial film 84 proceeds via the pyrolysis of  $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$  on the heated substrate 19 ( $400^\circ\text{C}$ ):



$\text{C}_2\text{H}_5\text{NCS}$  and  $(\text{C}_2\text{H}_5)_3\text{NCS}_2$  decompose into by-products such as  $\text{C}_2\text{H}_4$ ,  $\text{CS}_2$  and  $(\text{C}_2\text{H}_5)\text{NH}$  which are volatile in vacuum and therefore do not remain on the heated substrate 19 during the ZnS epitaxial film growth.

In this embodiment epitaxial film growth of ZnS was found on the Si (111) surface (lattice mismatch  $\sim 0.2\%$ ).

As shown in Figure 9, in one embodiment the growth of epitaxial films comprises the cleaning of the Si substrate (step 90), the heating of the Si substrate (step 92), the sublimation of the diethyldithiocarbamate precursor (step

94), the pyrolysis of the diethyldithiocarbamate molecules on the heated substrate (step 96) and the formation of the epitaxial ZnS film on the heated substrate (step 98).

The cleaning of the Si(111) substrates (step 90) in one embodiment comprises the sequence of steps outlined in Table 1.

1	annealing in oxygen	1050°C	30 min
2	rinse in deionised H <sub>2</sub> O	room temp (ultrasonic bath)	5 min
3	rinse in EtOH	room temp (ultrasonic bath)	5 min
4	rinse in Iso-propyl alcohol	room temp (ultrasonic bath)	5 min
5	N <sub>2</sub> blown dry		30 sec
6	12H <sub>2</sub> O : 7NHF <sub>4</sub> : 1HF	room temp	10 min
7	rinse in deionised H <sub>2</sub> O	room temp	1 min
8	N <sub>2</sub> blown dry		30 sec
9	5H <sub>2</sub> O : 1HCl : 1H <sub>2</sub> O <sub>2</sub>	80°C, oil bath	10 min
10	rinse in deionised H <sub>2</sub> O	room temp	1 min
11	N <sub>2</sub> blown dry		30 sec
12	12H <sub>2</sub> O : 7NHF <sub>4</sub> : 1HF	room temp	10 min
13	rinse in deionised H <sub>2</sub> O	room temp	1 min
14	N <sub>2</sub> blown dry		30 sec
15	5H <sub>2</sub> O : 1HCl : 1H <sub>2</sub> O <sub>2</sub>	80°C, oil bath	10 min
16	rinse in deionised H <sub>2</sub> O	room temp	1 min
17	N <sub>2</sub> blown dry		30 sec
18	12H <sub>2</sub> O : 7NHF <sub>4</sub> : 1HF	room temp	10 min
19	rinse in deionised H <sub>2</sub> O	room temp	1 min
20	N <sub>2</sub> blown dry		30 sec
21	5H <sub>2</sub> O : 1HCl : 1H <sub>2</sub> O <sub>2</sub>	80°C, oil bath	10 min
22	rinse in deionised H <sub>2</sub> O	room temp	1 min
23	N <sub>2</sub> blown dry		30 sec
24	NH <sub>4</sub> F (40%) or HF (5%)	room temp	10 min

25	rinse in absolute EtOH	room temp	2 min
26	Mounting onto sample holder/heater	16	
27	loading into deposition chamber	10	
28	heating for removing	350°C, vacuum ( $10^{-8}$ torr)	1
	surface contaminants		5
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			i
			n

In will be appreciated, however, that other cleaning step sequences and different treatment times may be applied, which may e.g. comprise sputtering and annealing steps in the high vacuum deposition chamber 10 (Figure 1).

#### Film Characterisation

The resulting epitaxial films were characterised using X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD).

Figure 2 shows an angle dependent XPD scan of the Zn  $2p_{3/2}$  intensity distribution for ZnS epitaxial films at thicknesses ranging from ~5 to 2000Å. The film thicknesses were estimated using the intensity attenuating of the XPS Si substrate peaks. The XPD measurements were performed after subsequent SSCVD deposition cycles.

The XPD patterns exhibit an intense and broad peaks 20, 22, and 24 at  $\theta=0^\circ$  which are the result of forward-scattering of Zn  $2p_{3/2}$  photoelectrons by neighbouring atoms. In ZnS, every zinc atom is surrounded by four sulfur atoms in a tetrahedral arrangement which results in either a cubic (sphalerite) or a, slightly distorted, hexagonal (wurtzite) structure.

The enhanced XPD intensities 20, 22, 24 at  $\theta=0^\circ$  in curves a, b, and c of Figure 2 respectively therefore indicate that the film molecules have preferred orientation at the film-to-substrate interface and the Zn  $2p_{3/2}$

5 photoelectrons are scattered by the sulfur neighbours perpendicular to the substrate.

As illustrated in Figure 3, the forward scattering enhancement 20, 22, 24 at  $\theta=0^\circ$  in curves a, b and c of Figure 2 is likely the result of forward-scattering of  
10 Zn $2p_{3/2}$  photoelectrons emitted from the zinc atoms 30 at the sulphur atoms 32, which are positioned directly above the zinc atoms 30 at a distance of 2.3 Å in an ideal ZnS cubic crystal structure.

In Figure 4, a XPS wide scan 40 for a typical ZnS epitaxial film embodying the present invention is shown.  
15 In the curve 40 shown in Figure 4, the silicon substrate peaks can also be observed, which are not fully attenuated due to the thinness of the ZnS epitaxial film on which the XPS measurement shown in Figure 4 was performed. The  
20 chemical composition obtained from XPS scans such as the one shown in Figure 4 were in agreement with those obtained for a ZnS reference sample.

In Figure 5, the curve 50 shows the XPD measurement for the 2000Å thick film of curve c of Figure 2 after Ar<sup>+</sup>  
25 ion etching.

During the Ar<sup>+</sup> ion etching, highly energetic (2000 electron Volt (2keV)) impact on the film surface, resulting in a disordering of the crystallographic structure of the surface. In curve 50 of Figure 5, the XPD scan therefore  
30 does not indicate a significant forward scattering enhancement at  $\theta=0^\circ$ .

Energy dependent XPD was employed to probe the in-plane orientation of the film molecules. The sample position and angle remained unchanged while the energy of  
35 the incoming X-rays was varied.

The energy dependent XPD features shown in Figure 6 are a result of diffraction of S 2p photoelectrons in the ZnS atomic network. The photoelectron take-off angle was 19° with respect to the surface plane, i.e. the measurement was sensitive for crystallographic order within the plane of the substrate. As diffraction is a long range order process (diffraction of photoelectrons requires single crystalline surfaces) the observation of peaks 60, 62, 64 demonstrates that the film is of epitaxial quality.

As illustrated in Figure 7, the peaks 60, 62, 64 in the measurement shown in Figure 6 are due to the forward scattering of S 2p photoelectrons emitted from the sulphur atoms 70 at zinc atoms 72, which are the next neighbours of the sulphur atoms 70 in the  $[11\bar{1}]$  crystallographic direction 74, along which the measurement shown in Figure 6 was measured. The distance between the sulfur atoms 60 and the Zn atoms 72 in an ideal ZnS cubic crystal structure is 2.3 Å.

In the following, a specific device application embodying the present invention will be described with reference to Figure 10.

Silicon is transparent at the typical telecommunications wavelength and it has been shown that Silicon-On-Insulator (SOI) structures can be used as waveguides. In these structures the wave is guided by a thin silicon layer on SiO<sub>2</sub>.

Figure 10 illustrates the principles of an optical modulator design 100. The silicon 102 is partially replaced by an epitaxial ZnS layer 104 which acts as waveguide. A suitable AC voltage applied across the ZnS layer 104 alters the refractive index of the ZnS and it is therefore possible to modulate light 105 guided through the film directly.

The epitaxial ZnS layer 104 is grown on the remaining slightly doped (111) oriented silicon layers 106 which also comprises the bottom electrode. A thin metal film 108



(e.g. Cr) is deposited onto the ZnS film 104 and form the top electrode. Optical losses are dependent on the density of defects in the ZnS layer 104 and it is therefore of significant advantage that they can be grown single

5 crystalline using the technology of the present invention.

It will be appreciated by a person skilled in the art that the present invention is not limited to that specific application, but other applications are possible, including for example in other optical modulator devices, optical  
10 waveguide devices, transistor and diode devices, blue light emitting devices, solar cells, and as coatings for infrared sensing, emitting, or transmitting devices.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due  
15 to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

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